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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>E21B 43/25</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/36668</b> <b>(43) International Publication Date:</b> 22 July 1999 (22.07.99)
<b>(21) International Application Number:</b> PCT/GB98/03863 <b>(22) International Filing Date:</b> 21 December 1998 (21.12.98)  <b>(30) Priority Data:</b> 9800942.6                      17 January 1998 (17.01.98)                      GB  <b>(71) Applicant (for all designated States except US):</b> AEA TECHNOLOGY PLC [GB/GB]; 329 Harwell, Didcot, Oxfordshire OX11 0RA (GB).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> WEBB, Philip, John, Charles [GB/GB]; Ault More, Stobhall, Maryculter, Aberdeenshire AB12 5GJ (GB).  <b>(74) Agent:</b> MANSFIELD, Peter, Turquand; AEA Technology plc, Patents Dept., 329 Harwell, Didcot, Oxfordshire OX11 0RA (GB).		<b>(81) Designated States:</b> AU, BR, CA, GB, MX, NO, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> WELL TREATMENT  <b>(57) Abstract</b>  Particles containing scale inhibitor may be made by contacting porous ceramic beads with a solution of scale inhibitor, and then drying the beads. If the dried beads are then contacted with a solution containing a high concentration of polyvalent cations, for example 2.5 M calcium ions, and then dried again, then the rate of release of scale inhibitor when the beads are subsequently contacted with water is reduced. Varying the concentration of the polyvalent cation in the range 0.1 to 5.0 M varies the rate at which the inhibitor is subsequently released. The beads may be used as fracture proppants or in a gravel pack so as to suppress scale formation in an oil or gas well.		

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Well Treatment

This invention relates to a method for treating an oil or gas well with oil field chemicals such as scale inhibitors, the chemicals being in a solid form on or in particles of insoluble material, to particles suitable for use in such a method, and to a method of making such particles.

10       The use of porous particles to introduce oil field chemicals into a well is known for example from GB 2 284 223 A, and from GB 2 298 440 A. The particles might be used in the form of a pre-packed screen, or might be used in a gravel packing process, or in a formation fracturing  
15       process. Such a process has been proposed in particular for introducing scale inhibitor. A method for making particles suitable for such use, but which need not be porous, is described in WO98/40606.

20       According to the present invention there is provided a method of making particles suitable for treating an oil or gas well wherein particles of an insoluble, inorganic material are wetted with a first solution comprising a well treatment agent in a solvent, the wetted particles  
25       are dried, the dried particles are then contacted with a second solution containing polyvalent cations at a high concentration, and the particles are then dried again.

      The cations in the second solution might be  
30       divalent, such as calcium ions, or trivalent, such as ferric ions. The concentration of the ions is preferably between 0.1 M and 5.0 M, for example between 2.0 M and 4.0 M. The quantity (number of moles) of the polyvalent cations in the second solution is preferably between 5  
35       and 20 times the quantity (number of moles) of the deposited well treatment agent in the particles. For

example for phosphonate scale inhibitor this mole ratio is preferably about 10:1, while for polymer type scale inhibitors it is preferably about 20:1. The volume of the second solution is preferably no more than that  
5 needed to wet the surfaces of the particles, for example about 0.36 ml of solution per gram of particles; the volume might be between 0.1 ml/g and 0.5 ml/g. If larger volumes of the second solution were to be used then there would be a greater degree of dissolution of the deposited  
10 well treatment agent, leading to formation of a less-adherent deposit. The aim is to modify the solubility of the deposited well treatment agent without changing its adherent character. The second solution is preferably an aqueous solution.

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The particles are preferably of a ceramic material, of generally spherical shape, and if they are porous they are preferably of porosity no more than about 30 percent, for example in the range 10 percent to 20 percent. They  
20 are typically of size between about 0.3 mm to 5.0 mm, more preferably between 0.5 mm and 2.0 mm for example 1.0 mm. They may be supplied into the well packed into a pre-packed screen in the form of a filter bed, or may be used as a gravel pack within the oil well and the  
25 perforations, or alternatively if the particles are sufficiently strong they may be used as fracture proppants in a fracture process and thereby be injected into cracks in the formation extending away from the well bore. The treated particles may be used on their own, or  
30 may be mixed with other particles which may be non-porous or may be porous and contain other oil field chemicals.

The particles preferably comply with the standards set out in the API recommended practices for testing for  
35 gravel material, or those for proppant material (depending on how they are to be used). These specify

criteria for particle shape, for acid resistance, and for crush resistance. The criteria for crushing strength depend on the particle size; for example particles of size 20-40 mesh (0.42 - 0.84 mm) for use as proppants must not lose more than 14 percent by mass at a closure pressure of 4000 psi (28 MPa).

After the particles have been made as described above, they may be further coated with a polymer or resin coating, which will modify the rate of dissolution.

The invention will now be further described by way of example only, and with reference to the accompanying drawings in which:

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Figure 1 shows graphically, on a linear scale for concentration, the release of a scale inhibitor from particles made according to the invention, compared to those made by a known process;

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Figure 2 shows graphically, on a logarithmic scale for concentration, the same comparison as in figure 1 but for a considerably longer time scale.

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When it is desired to enhance the permeability of a formation comprising oil-bearing strata in the vicinity of an oil well, it is known to inject a fluid into the well such that the pressure at the depth of those strata is sufficient to cause fracturing of the rocks of the strata. The fluid injected into the rocks may contain a dissolved polymer which may be cross-linked to form a gel (so it is of high viscosity), and may include particles of solid material such as sand grains or ceramic spheres which are carried into the fractures by the injected fluid. When the pressure is reduced the particles prevent the fractures closing. Such particles may be

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referred to as proppant particles. Typically the fractures may extend as much as 20 m or even 50 m or more out from the well bore, and the proppant particles will be distributed throughout the length of each fracture.

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Where a producing section of an oil well extends through a poorly consolidated formation (or stratum) it is known to prevent inflow of sand particles from the formation by means of a gravel pack. This consists of a  
10 filter bed of small particles filling all the space between a tubular fluid-permeable screen within the well bore, and the wall of the well, and extending into the perforations, the particles preferably being between 5 and 6 times larger than the sand particles whose inflow  
15 is to be prevented. Such particles are usually referred to as gravel, although they may be substantially identical to those referred to as proppants; as a general rule particles for use as gravel do not have to be as strong as those for use as proppants.

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The particles for use in such gravel pack or fracture processes may be ceramic beads of generally spherical shape, for example of diameter 0.7 mm, and of porosity 15 percent.

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#### Example 1

The beads can be impregnated with a scale inhibitor by substantially the same procedure as that described in  
30 GB 2 298 440 A, as follows:

(i) concentrated scale inhibitor is made from a commercially-available diethylene-triamine penta-(methylenephosphonic acid)-based scale inhibitor  
35 (initially about 25 percent active material), by first



adding to this inhibitor 5 000 to 25 000 ppm cations (calcium and magnesium) added as chlorides, preferably 12 000 to 25 000 ppm, and then distilling under vacuum to about half the initial volume. The scale inhibitor may be referred to as DTPMP. The pH is adjusted to a value in the range pH 6.0 to pH 11.0 by adding concentrated sodium hydroxide, preferably to pH 10.

(ii) the ceramic beads are placed in a pressure vessel, and the vessel evacuated to about 0.1 mbar (10 Pa) absolute to ensure no air or vapours remain in the pores. The vessel is then filled under vacuum with the concentrated inhibitor. After quarter of an hour the vacuum is released, the vessel drained, and the wet beads removed.

(iii) the wet beads are then dried in an oven or a fluidised bed.

The impregnated particles are then subjected to two further steps:

(iv) the dried beads are then contacted with a small volume of an aqueous solution of calcium chloride containing 100 grams per litre of calcium ions (2.5 M of calcium ions), the volume of the solution being just sufficient to wet the surfaces of the beads. The volume of solution is about 18 ml to wet 100g of the dried beads.

(v) the wetted beads are then dried by heating in a rotary drier or an oven at 120°C.

Experimental measurements were then made using three columns packed with impregnated beads, and passing sea water through the columns. Referring now to figure 1,

experimental measurements are shown of the concentration of the scale inhibitor (DTPMP) in the water emerging from the bed of particles, the inhibitor concentration being plotted on a linear scale, for different numbers of column pore volumes which have flowed through the column. The three columns contained beads which had been treated in different ways: graph A shows the results obtained using beads made as described above; graphs B and C show the results obtained using beads impregnated as described in steps (i) to (iii) above but without the subsequent steps, the scale inhibitor solution being at pH 8 (graph B) and pH 10 (graph C) respectively. Referring now to figure 2 this shows graphically the same measurements but with a logarithmic scale for the inhibitor concentration, and continuing to much larger numbers of column pore volumes.

It will be observed from these graphs that the beads treated as described above in steps (iv) and (v) release the inhibitor much more slowly than the beads which were not so treated. In most applications the required scale inhibitor concentration is no more than 100 ppm (typically in the range 0.1-100 ppm) so that the observed values of scale inhibitor concentration with these treated beads would certainly be adequate to prevent scaling. Because the very large initial inhibitor release does not occur, inhibitor can be expected to be released at an adequate concentration for a considerably longer period of time.

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The treatment solution of step (iv) may differ from that described above for example containing a different polyvalent cation such as iron, or chromium, or aluminium; and the concentration of the polyvalent cations may differ from that specified above for example it might be 100 grams per litre of iron (that is 1.8 M).

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The cations are preferably at a concentration between 0.1 M and 5.0 M. As described above the beads were merely contacted with the calcium-containing solution, relying on imbibition of the solution into the pores of the proppant. Alternatively, vacuum impregnation can again be used (as in step (ii)) to promote contact between the solution and the solid scale inhibitor in the pores of the proppant.

10 The high initial dissolution rate observed above in graphs B and C is commonly observed with solid scale inhibitors, for example alkali metal (e.g. Na or K) or alkaline earth metal (e.g. Ca or Mg) salts of DTPMP, phosphino-carboxylic acid, polyvinyl sulphonate, 15 polyacrylate, vinyl sulphonate and acrylic acid copolymer, maleic and acrylic acid copolymer, or other phosphonate-type inhibitors such as aminotrimethylene phosphonic acid. The initial concentrations are typically in the range 1 000 - 100 000 ppm. The high 20 release rates are believed to be attributable to the heterogeneous composition of the solid scale inhibitor; compositions with relatively high alkali metal and low alkaline earth metal content dissolve preferentially when in contact with brine or water, whereas the dissolution 25 of scale inhibitor compositions with relatively high alkaline earth metal content is slower. Hence when depositing scale inhibitor from solution, as in step (ii) above, it is preferable to add cations such as calcium and/or magnesium at a concentration preferably in the 30 range 5 000 to 150 000 ppm, and as the mole ratio of polyvalent cations to scale inhibitor is increased in the solution from which the inhibitor is deposited, the concentration of scale inhibitor in water subsequently flowing past the beads decreases. The pH of the solution 35 also affects the composition of the deposited scale inhibitor, and so affects the subsequent rate of

dissolution of the inhibitor. Increasing the pH of the solution reduces the rate of release of the inhibitor subsequently, so the pH is generally adjusted to be in the range 6 to 11. Changing the composition of the deposited scale inhibitor in these ways affects the long-term release rates, but does not prevent the high initial release. Treating the deposited scale inhibitor with polyvalent cations as in step (iv) above does however effectively suppress this initial release.

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### Example 2

In an alternative example the scale inhibitor initially deposited contains no alkaline earth metal ions. The procedure is as follows:

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(i) 500 ml commercially available concentrated DTPMP scale inhibitor (47% active inhibitor) is adjusted to between pH 10 and pH 11 by adding 260 ml 50 weight percent sodium hydroxide, at below 45°C.

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(ii) porous ceramic beads of 9% porosity are vacuum impregnated with this inhibitor solution as described in Example 1.

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(iii) the wet beads are then dried at 110°C, and if necessary loosened to be free-flowing, and sieved to remove any fines. Typically 100 g of the dried beds contain about 2 g of DTPMP.

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(iv) the dried beads are then contacted with a small volume of an aqueous solution of calcium chloride, 50% by weight of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (this is about 4.7 M). As described in Example 1, the volume of this solution is just enough to wet the surfaces of the beads; in this case it was about 16 ml to wet 100 g of the dried beads.

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(v) the wetted beads are then dried at 110°C, and if necessary are then loosened to be free-flowing and sieved to remove any fines.

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The drying steps (iii) and (v) may be performed in a counter current rotary convective dryer, and this provides a free-flowing product. The contacting step (iv) may be performed by exposing the dried beads to an atomised spray mist of the concentrated calcium salt solution.

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### Example 3

The initially-deposited inhibitor might instead contain only one type of alkaline earth metal. One such example is as follows:

(i) 500 ml commercially-available DTPMP scale inhibitor (47% active inhibitor of molar mass 567 g) is mixed with 260 ml 50 weight per cent NaOH solution, 82 ml distilled water, and 84.2 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (solid). This corresponds to one mole of calcium ions to one mole of DTPMP.

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The subsequent steps are as in Example 2. The dried beads, of 9% porosity, typically contain about 1.5 g of DTPMP per 100 g of beads.

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### Example 4

It will also be appreciated that the invention is applicable with other types of scale inhibitor. One such example is as follows:

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(i) 500 ml commercially available concentrated phosphino-carboxylic acid (PCA) polymer scale inhibitor (40% active inhibitor of molar mass about 1900 g) is mixed with 24.7 g NaOH (solid), 18.7 g Ca(OH)<sub>2</sub> (solid) and 5 125 ml distilled water. (The resulting solution consequently contains about 14000 ppm of calcium ions). This corresponds to two moles of calcium ions to one mole of PCA polymer.

10 The subsequent steps are as in Example 2. The dried beads, of 9% porosity, typically contain about 2 g PCA polymer per 100 g of beads.

Claims

1. A method of making particles suitable for treating an oil or gas well wherein particles of insoluble, inorganic material are wetted with a first solution comprising a well treatment agent in a solvent, the wetted particles are dried, the dried particles are then contacted with a second solution containing polyvalent cations at a high concentration, and the particles are then dried again.
2. A method as claimed in claim 1 wherein the polyvalent cations in the second solution are ions of calcium or iron.
3. A method as claimed in claim 1 or claim 2 wherein the concentration of the polyvalent cations in the second solution is above 1.0 M.
4. A method as claimed in claim 3 wherein the concentration is between 1.5 and 5.0 M.
5. A method as claimed in any one of the preceding claims wherein the particles are of a ceramic material, of generally spherical shape, and of porosity no more than about 30 percent.
6. A method as claimed in any one of the preceding claims wherein the first solution, comprising the well treatment agent, also contains polyvalent cations at a concentration in the range 5 000 to 150 000 ppm.
7. Particles made by a method as claimed in any one of the preceding claims.
8. A method of treating an oil or gas well with a well treatment agent, wherein particles as claimed in claim 7

and comprising the well treatment agent, are introduced into the well.

9. A method as claimed in claim 8 wherein the particles  
5 are used as fracture proppants.



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Fig.1.

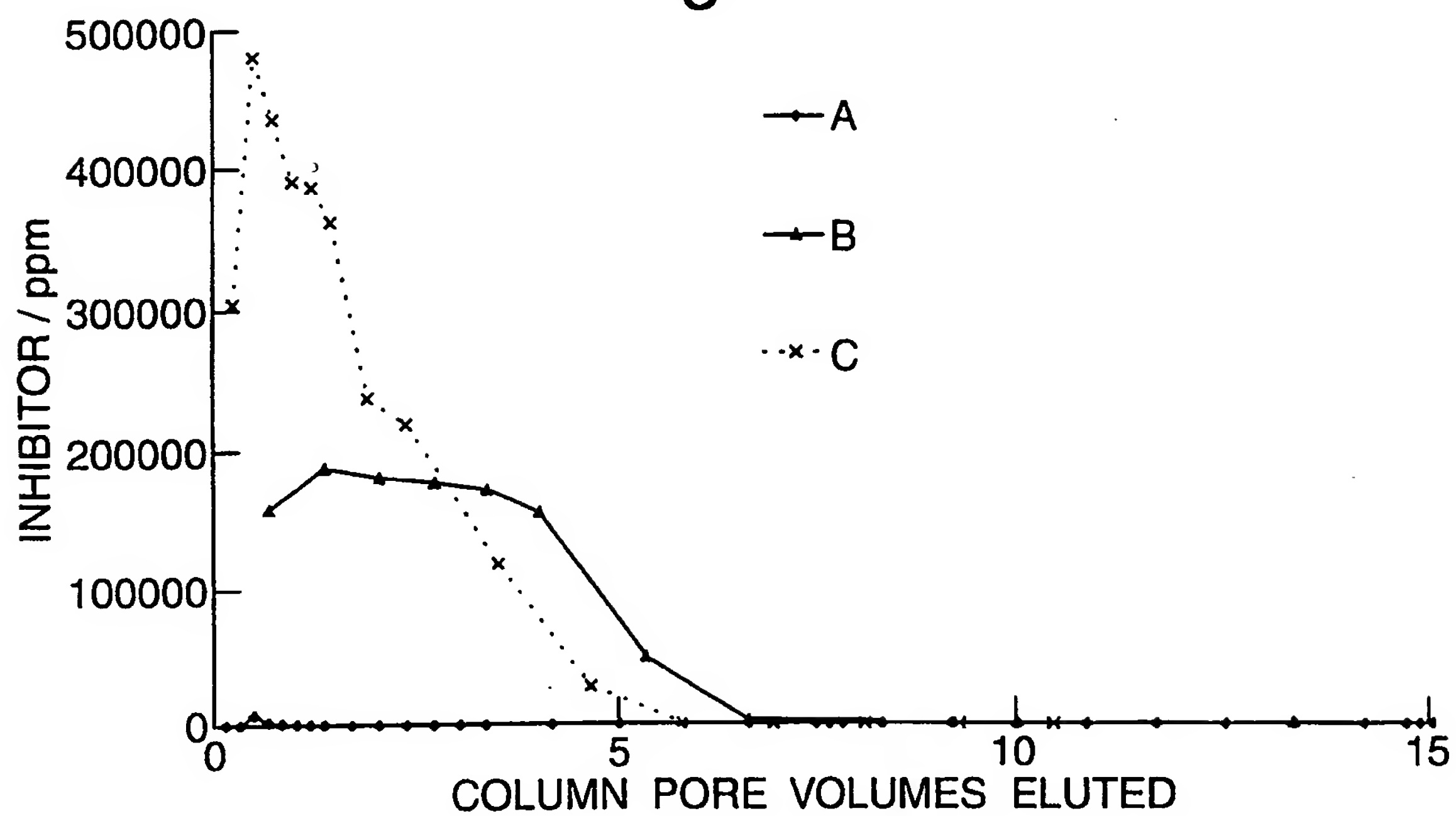
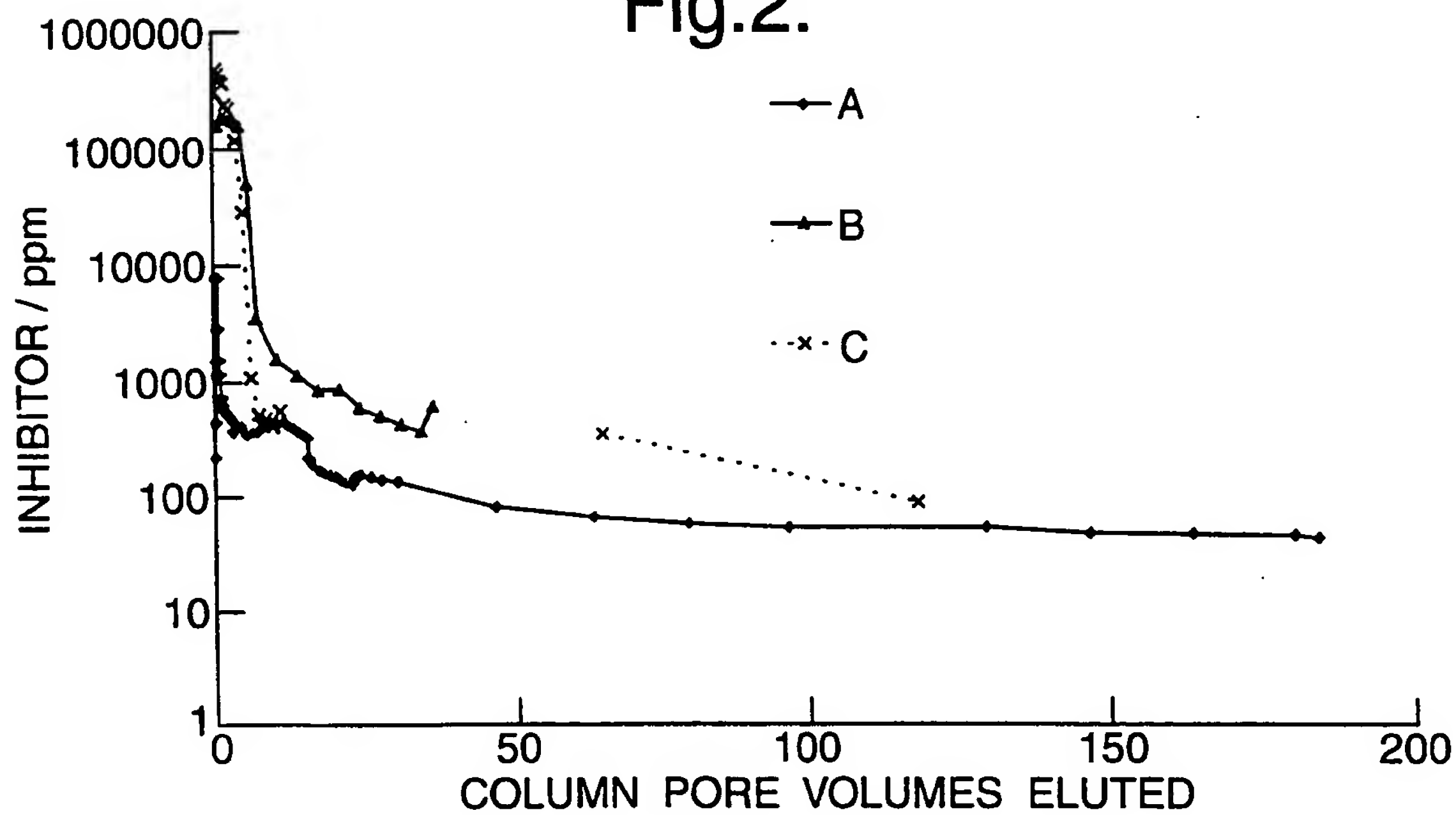


Fig.2.



# INTERNATIONAL SEARCH REPORT

Intern .al Application No

PCT/GB 98/03863

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 E21B43/25

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 298 440 A (UNITED KINGDOM ATOMIC ENERGY AUTHORITY) 4 September 1996 cited in the application see page 6, line 13 - line 25 ---	1,5-9
P,A	WO 98 40606 A (AEA TECHNOLOGY PLC) 17 September 1998 see page 2, line 26 - line 33 see page 4, line 23 - page 5, line 21; claims 1,3,4 -----	1,5-9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

26 February 1999

Date of mailing of the international search report

09/03/1999

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Information on patent family members

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